

SPECTROSCOPIC STUDIES OF PHYSICO-CHEMICAL EFFECTS
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During recent years, a considerable volume of literature has appeared dealing with pressure studies. In spite of all this work, very little is actually known of the chemical effects, on a molecular level, produced by high pressure. This lack of knowledge stems from the previous necessity of determining changes almost exclusively by postmortem examination of the pressurized material. Obviously, if no permanent phase change or reaction occurred, no pressure effect could be determined.

Battelle has pioneered in the utilization of commercially available equipment for infrared spectroscopic in situ monitoring of changes in liquids under ultra-high pressures. These techniques are now applicable to almost any liquid or solid sample, and potential applications have been shown to bridge virtually every area of physical-chemical endeavor.

It is easily demonstrated, by changes in the infrared spectrum as a sample is pressurized, that moderate pressures of 20 to 50 kilobars can produce significant, but completely reversible, effects on molecular structure. Definitive interpretation of these changes have exciting ramifications in every aspect of chemical knowledge. However, the broad spectrum of pressure studies can be grouped into three phenomenological areas:

1. Phase Behavior. Most liquid solidify under pressure, with polymorphism the rule rather than the exception (even the simple benzene molecule has at least two solid phases and we obtained a "plastic crystal" form of benzene under pressure. High-pressure, high-temperature polymorphic transitions are known for many, if not most, solids, as the eight forms of ice, five forms of ammonium nitrate, or seven forms of tripalmitin. In situ measurements will reveal new phases undetectable by conventional postmortem examinations of quenched samples.

Infrared spectroscopy has played an important role in solid-state studies. While the infrared spectrum is usually characteristic of a particular polymorphic form, it is particularly sensitive to any modification of molecular shape such as rotational isomerism, tautomerism, or conformational differences which may be encountered in high-pressure phases.

2. Intermolecular Forces. Fascinating possibilities for elucidating intermolecular interactions in condensed phases are offered by controlled variation of pressure from ambient to 100 kilobars, and of temperature from ambient to 400 C, on a sample of determinable volume. Questions of particular chemical importance which can now be approached experimentally are:

(a) At what point do repulsive intermolecular forces exert an appreciable influence on intramolecular forces? For example,

most intramolecular vibrations in condensed phases shift to higher frequencies with increasing pressure. Is this shift simply a dielectric effect related to increasing density with compression, or does it actually represent a decrease in bond length of the particular vibrating entity? While there will be a dielectric effect with compression, evidence from studies of hydrogen-bonded compounds indicates that bond lengths are definitely affected.

(b) When compressions are sufficient to result in decreased intramolecular bond lengths, is the shortened bond more, or less, chemically active? Do polar bonds behave the same as less polar bonds under similar conditions?

(c) Does order or orientation in the liquid approach the order in a corresponding solid as the density of the pressurized liquid approaches the density of that solid? Techniques developed for measuring compressibilities with photomicrographic and infrared spectroscopic data were used to show that some liquid halogenated ethanes compress to the density of the solid before solidification occurs. Also, the pressure behavior of strongly hydrogen bonded liquids indicates a higher degree of order than was previously suspected.

3. Synthesis. Novel syntheses are possible in pressurized systems. For example, we have successfully polymerized a conjugated aromatic substituted acetylenic compound by UV irradiation of a high-pressure solid phase. Reaction was not induced in either the ambient or pressurized liquid phases, nor in a low-temperature solid phase of the material.

These techniques are described and the value of in situ capabilities is demonstrated by completely reversible pressure effects which cannot be detected by post mortem examination. These techniques involve using a diamond anvil high-pressure cell fitted with a metal gasket to contain the liquid. The very small aperture of the diamond cell greatly limits the energy available to the spectrometer and requires unusual instrumental conditions to achieve reliable results. The determination of these operating conditions and their effect on spectral results is discussed. These spectral results clearly show that much more than simple close-packing of molecules is involved at pressures of 10-100 kilobars. It is a great aid in pressure studies to be able to observe by normal optical microscopy any corresponding changes in the physical state of the sample. This is particularly true for the study of organic liquids, many of which solidify at relatively low pressures. This phenomenon has been used in the easily manipulated diamond cell to grow single crystals, quickly and easily, of many organic compounds. The powerful combination of infrared spectroscopic and optical microscopic monitoring allows some very interesting comparisons of these high-pressure single crystals with normal crystals produced by freezing.

Spectra will be shown of various ranks of coal obtained by high-pressure techniques. These spectra will be discussed both in terms of a routine sampling method for qualitative identification and in terms of new knowledge to be gained concerning the structure of coals.